Abstract No. over648

The Electron Density Distribution in a Tetra-nuclear Iron(III) bis(μ^3-oxo) Butterfly-like Compound, $[Fe_4^{III}O_2(C_5H_9O_2)_8(C_6H_7N)_2]\cdot 2CH_3CN$

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Beamline(s): X3A1

Introduction: In our investigation of tri-nuclear oxo-centered iron compounds [1], we encountered an interesting side-product, $[Fe_4^{III}O_2(C_5H_9O_2)_8(C_6H_7N)_2]\cdot 2CH_3CN$. This compound exhibits two equivalent $Fe_3(\mu^3\text{-}O)$ environments, which are suitable for comparison with the previously studied bonding environments in the trinuclear carboxylates [2].

Methods and Materials: Synchrotron X-ray diffraction data for the title compound were collected with a Bruker SMART 6000 CCD detector at beamline X3A1 using a liquid He-cooling device to reach an experimental temperature of 16(5) K. 55130 reflections were integrated, giving 20960 unique reflections with an internal agreement of R_{int}=0.025. The electron density distribution (EDD) in the complex was modelled employing a multipolar model to give $R(F^2)$=0.029 for 715 parameters.

Results: In contrast to observations in the trinuclear complexes, the EDD in the title complex shows two very significantly different Fe^{III}-(μ^3-O) interactions, the shorter Fe(2)-O(1) being very directional with a large accumulation of electron density in the bond, while the longer Fe(1)-O(1) interaction is more diffuse (Figure 2). Furthermore, Fe(1) is bonded to both μ^3-O atoms, which exhibit an unusually short separation of 2.532(1) Å, see Figure 1. Topological analysis of the experimental EDD reveals a polarization of the valence electrons on the μ^3-O into the O(1)-O(1) direction. A similar observation of enhanced interaction between two metal-bridging oxygens has been made previously from low-resolution synchrotron X-ray data [3].

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References:

[1] C. Wilson, *et al.*, *J. Am. Chem. Soc.* (2000), *122*, 11370-11379
[2] J. Overgaard, Ph. D. thesis, Department of Chemistry, University of Aarhus, Denmark, 2001.
[3] A. F. Jensen, *et al.*, *Inorg. Chem.* (1995), *34*, 4244-4252

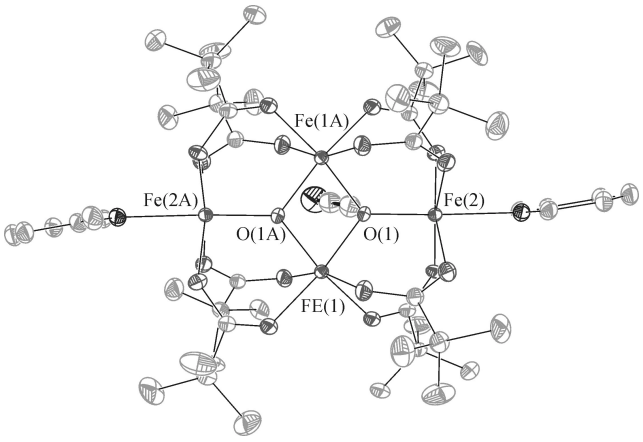

Figure 1. Thermal ellipsoids plots showing 90% probability surfaces.

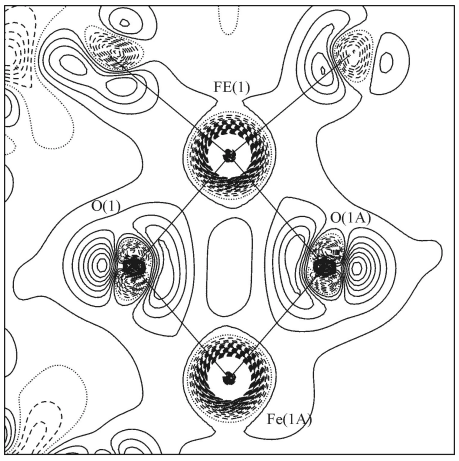

Figure 2. Deformation density in the central Fe(1)-O(1)-Fe(1)-O(1) region. Contours at ±0.1 eÅ^{-3}.